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Research Article

SYNTHESIS, CHARACTERIZATION OF A NOVEL ADSORBENT, POLYANILINE-ZR(IV)-IODOPHOSPHATE AND ITS APPLICATION FOR THE REMOVAL OF PB (II) FROM AQUEOUS SOLUTION: ISOTHERMS, KINETICS, THERMODYNAMICS AND DESORPTION STUDIES

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ABSTRACT

A novel composite, polyaniline-Zr(IV)-iodophosphate (PZIP) was successfully synthesized by simple, suitable, Sol-Gel method and was explored as an adsorbent for the removal of Pb (II) from aqueous solution using batch method. The adsorbent was characterized by advanced sophisticated techniques like FT-IR, TGA-DTA, XRD and SEM. The adsorbent was fairly stable against many chemical reagents like HCl, H_2SO_4, and NaOH. The optimum condition for the maximum adsorptive removal of Pb (II) ions from aqueous solution was determined as a function of contact time, pH, adsorbent dose, and temperature. The pH and temperature played an important role on the adsorption of Pb (II) ion from aqueous solution. The kinetic data well fitted to pseudo first order and pseudo second order kinetic models. The Langmuir and Freundlich isotherm describes the adsorption behavior. The maximum adsorption capacities obtained from Langmuir and Freundlich models are very close to experimental value (17.91 mgg^{-1}). Thermodynamic parameters suggested that the adsorption of Pb (II) onto PZIP was physical, endothermic, and spontaneous in nature and involves the weak forces of attraction. The adsorbent was found very effective in the removal of Pb (II) from aqueous solution it was successfully regenerated and showing 80% of Pb (II) removal after the regenerated in third cycle. Therefore based on the above result it may be concluded that poly aniline Zirconium (IV) iodo phosphate (PZIP) could be a promising adsorbent in treating water contaminated with Pb (II).

INTRODUCTION

Now a days, water pollution is world's most severe environmental concern. The main reason of water pollution is the discharging of inappropriate treated industrial effluents containing toxic pollutants resulting from the numerous human activities. These pollutants enter into various nearby environmental water resources and finally reach to main streams. They are threatening not only the environment but also the human health especially to our water sources. So it has become the center of attention among the researchers working in the direction of water treatment as pollutants may be hazardous for human health and animals even at small concentrations. In the recent years, water pollution due to toxic heavy metals has been a major cause of concern among researchers[1].There are more than twenty heavy metal ions, but As (III), Cd (II), Cr (III), Cr (VI), Pb (II), and Hg (II) in the environment are of special concern due to their toxicity to many life forms. The organic pollutants are liable to biological degradation which can degrade into harmless end products, but heavy metal ions do not undergo degradation. Heavy metals and other toxic pollutants are considered enormously mean since they are noxious, non-degradable, and insistent in the environment[2]. Heavy metals when introduced into water; it may remain either in dissolved form or are leached down with extra water, or else partially fixed for the time being or permanently in sediments. Some elements move downward through the deposit polluted ground water, which is often consumed by humans in many ways, so they may be harmful to humans and animals[2-4]. The lead holds the topmost place among these most toxic metals in the list that may bio-accumulate in the human body. It has been reported that the maximum permissible limit of Pb (II) in potable water is about 10 μg L^{-1}[5]. The Lead consumption above its permitted limit for a long term may cause mental retardation, kidney disease and anemia, inhibition of hemoglobin formation, abortion, hypertension, learning disabilities, kidney damage, and mental retardation etc.[6-9]. Battery manufacturing, fossil fuels, photographic materials, pigments, printing, pulp and paper industries, lead smelter, boat and ship fuels, and ammunition

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industries are the major source of lead[10, 11]. Therefore, taking into account the hazardous effect of lead, new adsorbent for removal of trace amount of Pb (II) from the contaminated water resources is very important. Various techniques like adsorption, bio-filtration, chemical precipitation, ion exchange, and nano-filtration have been employed to remove lead from waste water [12-14]. Among these techniques adsorption has appeared as an active and reasonable technique for treating water and industrial wastewater containing metal ions, contributing substantial benefits comprising low cost, ease of availability, operation and efficiency, as compared to physical, chemical and biological techniques. The most important advantage of adsorption technique is that there is no formation of hazardous side products. Researchers have developed various adsorbents such as H_2O_2 oxidized Activated carbon, Oxidized MWCNTs, Oak bar char, Cicerartientinum bio-mass, Organobentonite, toeliminate the lead from aqueous solution[16-20]. This research work deals with the synthesis, characterization, and optimization of parameters(effect of pH, adsorbent dose, effect of initial metal ion concentration),effect of temperature and contact time, in order to maximum adsorptive elimination of lead (II) from aqueous solution. This work also deals with kinetics, isotherms and thermodynamics. The adsorbent shows a high potential for removal of lead (II) from aqueous solution.

MATERIALS AND METHODS

Chemical Reagents

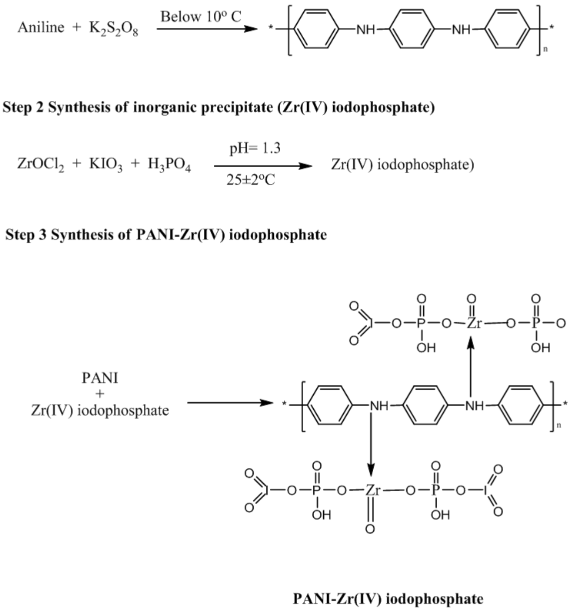
The reagents used for the synthesis of composite material were Aniline (S D Fine-Chem ltd. Mumbai), Zirconium oxychloride octahydrated (Otto Chemie. Mumbai, India), Potassium iodate (Merck, Mumbai, India). All other chemicals used for the preparation of reagent solutions were of analytical reagent grade. $Pb(NO_3)_2$ was obtained from Thomas Baker, Mumbai. All working solutions were prepared in double distilled water. A stock solution of metal ion of interest was prepared by dissolving appropriate amount of reagent in double distilled water in 1 L standard volumetric flask. Further, the desired concentrations of adsorb ate were obtained by diluting the stock solution with double distilled water. The pH of the working solutions was maintained by using HNO_3 and NaOH.

Instruments

Atomic Absorption Spectrometer (AAS) GBC Avanta Ver. 1.33, FTIR spectrophotometer (Interspec 2020, spectrolab, UK), DTG 60H Shimadzu thermal analyzer in nitrogen atmosphere at the rate of 10 (C min^{-1}), Scanning electron microscope (JEOL JSM-6510LV), X-ray Diffractometer (PW 3050/60; X'PRO-PAN analytical, Netherland) with Cu Kα´ radiation (α´= 1.54 A°), and Systronics µ pH system 361.

Synthesis of polyaniline-Zr(IV)-iodophosphate: (PZIP)

The synthesis of adsorbent was carried out in two steps using the sol-gel method. In the first step organic part polyaniline, a dark green color gel was prepared by mixing equimolar solutions of ammonium persulphate (prepared in 1 M HCl), with 10% aniline double distilled (prepared in 1 M HCl) byconstant stirring on a magnetic stirrer at ±4 ℃ . In the second step, inorganic part zirconium (IV) iodophosphate was prepared by mixing equi molar of zirconium oxychloride with potassium iodate solution and orthophosphoric acid solution at room temperature; a white gelatinous precipitate was formed. The organic part i.e. polyaniline was mixed with the white gelatinous precipitate of zirconium (IV) iodophosphate. The pH of the resulting mixture was adjusted to 1 and stirred on a magnetic stirrer for 6 h. The resultant product was left at room temperature for 24 h for digestion, then filtered and washed with excess amount of distilled water to remove excess acid from it. The washed gel was dried in an oven at 50 °Cand ground into fine powder, finally stored in a desiccator for further used. The schematic presentation of overall synthesis is given by Scheme 1.



Scheme 1schematic presentation for the synthesis of polyaniline-Zr(IV)-iodophosphate.

Adsorption experiments

Adsorption experiments were performed in batch to find the effect of pH, adsorbent dose, contact time, initial dye concentration, and temperature on the adsorption of lead (II) ion on the adsorbent by changingone parameter under study and keeping others constant. In each experiment 0.02 g adsorbent was placed in a 150 ml conical flask containing 20 mL of the desired concentration of adsorbate solution. In each experiment the resulting mixture was shaken in temperature controlled shaker incubator and then filtered with Whatman filter 41. The remaining concentration of the filtrate solution was determined by Atomic Absorption Spectrometer. The percentage and amount of adsorbate on the adsorbent was calculated bythe following Eq. (1) and Eq. (2):

$$\%\ \text{Removal} = \frac{(C_i - C_e)}{C_e} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (2)$$

where, $C_i$initial and C_e **Table** concentration (mgL^{-1}) of the adsorbate in solution at equilibrium, q_e is the quantity of adsorbate adsorbed on the adsorbent at the time of equilibrium (mgg^{-1}), V is the volume of adsorbate solution taken (L), W is the mass of adsorbent (g).

Characterization of the adsorbent

In order to know crystalline or amorphous nature of the adsorbent X-Ray diffraction analysis was carried out. The FT-IR analysis of adsorbent was done to identify the functional groups taking part in the adsorption of the lead (II) ions before and after the adsorption process. The surface analysis of the adsorbent before and after the adsorption was recorded by Scanning Electron Microscope.

Effect of contact time and initial concentration

The time essential to complete the adsorption process is a very important factor in order to save experimental time. In order to understand the effect of initial metal ion concentration experiments were done using the batch method at room temperature. 0.02 g of adsorbent was added to 20 mL solution of various initial concentrations of lead (II) ion (10-100mgL^{-1}). After specified time interval samples were filtered using Whatman filter paper number 41, residual concentration of the metal ions in the filtrate was analyzed after preset contact time. The effect of contact time was performed with 50 mgL^{-1} metal concentration, 0.02 g adsorbent in 20 mL at pH 7 from 5 to 200 min. and the remaining concentration of the filtrate at particular time was determined by AAS.

Effect of pH

The adsorption capacity of the adsorbent is greatly affected by the pH of the adsorbate solution because H^+ and OH^- ions are adsorbed quite intensely, therefore pH of the solution has influence on the adsorption of other ions. To examine the pH effect on the adsorption of lead (II) ions on the adsorbent, the pH of a series of conical flasks containing 20 mL of adsorbate solution over the pH range from 1-7which was adjusted using HNO_3 and NaOH solution and 0.02 g of adsorbent was added to the solution. After fix time interval the remaining concentration of filtrate was determined by AAS.

Effect of adsorbent amount

The dependence of Pb (II) adsorption on the amount of adsorbent was studied at different amount of adsorbent over the range 0.02-0.2g in batch method with 20 mL of 50 mgL^{-1}Pb (II) solution.

Chemical stability

In order to use the synthesized material as a potential adsorbent it was tested with water, diluted acids of HCL and H_2SO_4 and bases like NaOH for its chemical stability. The adsorbent PZIP was found to be stable in water, dilute acids and bases. For this 0.02 g of PZIP was placed in a conical flask containing 20 ml of concerned chemical. It was found that the material was fairly stable against these chemicals.

RESULTS AND DISCUSSION

Characterization of the adsorbent

The functional groups or binding sites responsible for the adsorption of lead (II) ions from the aqueous solution were identified by FTIR spectra before and after the adsorption to understand the surface binding mechanism. The FTIR spectra of Zr(IV)-iodophosphate, polyaniline-Zr(IV)-iodophosphate composite before and after the adsorption of lead (II) ions respectively was recorded(Fig. 1).

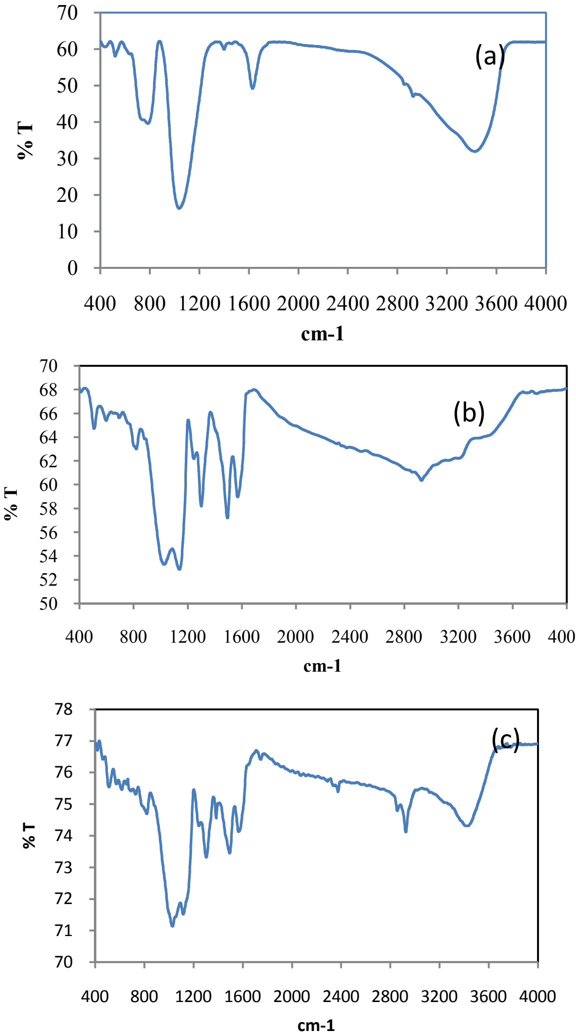


Fig. 1 FT-IR spectra of (**a**) Zr (IV) iodo-phosphate (**b**) Poly-aniline Zr (IV) iodo phosphate composite (**c**) Pb (II) adsorbed onto the Poly-aniline Zr (IV) iodo phosphate.

Peaks appears in the region 3429 cm^{-1} and 2927 cm^{-1}may be attributed to stretching vibrational band of hydroxyl (–OH) and vibrational bands of aliphatic C–H respectively. A sharp peak at 1036 cm^{-1} is due stretching of phosphate group. The Peak at 784 cm^{-1}(Fig.1a) may be assigned to iodate group. The FTIR spectrum of adsorbent before the Pb (II) adsorption (Fig. 1b) revealed two characteristic peaks for PANIat 1493 and 1569 cm^{-1} may beascribed to the C=N stretchingand C=C stretching of quinoid (Q) rings andbenzenoid (B) rings, respectively[21, 22, 24]. The peaks at 1300 and 1139 cm^{-1} may be ascribed to distortion vibration of metal hydroxyl group and corresponding metal phosphate respectively [23-24]. The peak at 1380 cm^{-1} may be due to presence of nitrate. The peak appearing at 820 cm^{-1} confirms the presence of iodate group [21]. The Zr–O stretching vibrational peaks appears in the region 626-447 cm^{-1}[25]. It is obvious from the (Fig. 1c), the adsorption of Pb (II) ions at the surface of adsorbent was also confirmed by the appearance of new peak and there were remarkable shifts in the frequency of peaks related with the treated adsorbent, which indicates that there are sufficient number of surface active functional groups which accounts for the high potential for adsorption of PZIP.

Scanning Electron Microscopy

The SEM analysis provides appropriate surface morphological information of the adsorbent. The surface of the adsorbent was found sufficiently irregular, rough and porous, which provides suitable binding sites for the adsorbate. The SEM images (Fig. 2) of the adsorbent before and after the adsorption of lead (II) was recorded. It is very clear (Fig.2aand2b) that the morphology of the adsorbent was considerably changed after the adsorption of Pb(II) ions. EDX analysis spectra (Fig.3a and 3b) were recorded before and after the adsorption of Pb (II) ion onto adsorbent, confirmed the synthesis of PZIP and PZIP- Pb (II) system.

X-Ray diffraction and thermal analysis

The characteristic XRD diffraction pattern of adsorbent revealed that the adsorbent has amorphous nature (Fig. 4a). The thermal behavior of PZIP composite was studied over the temperature range of 0-600 °C.The thermogram (Fig. 4b) of the adsorbent revealed two steps weight loss, first weight loss (18.538 %) below 400 °C may be contributed to the unbound and physically adsorbed water. The second minor weight loss (4.513 %) was observed below 600 °C may be attributed to other probably volatile substances. The thermal analysis showed that the adsorbent is stable at higher temperatures.

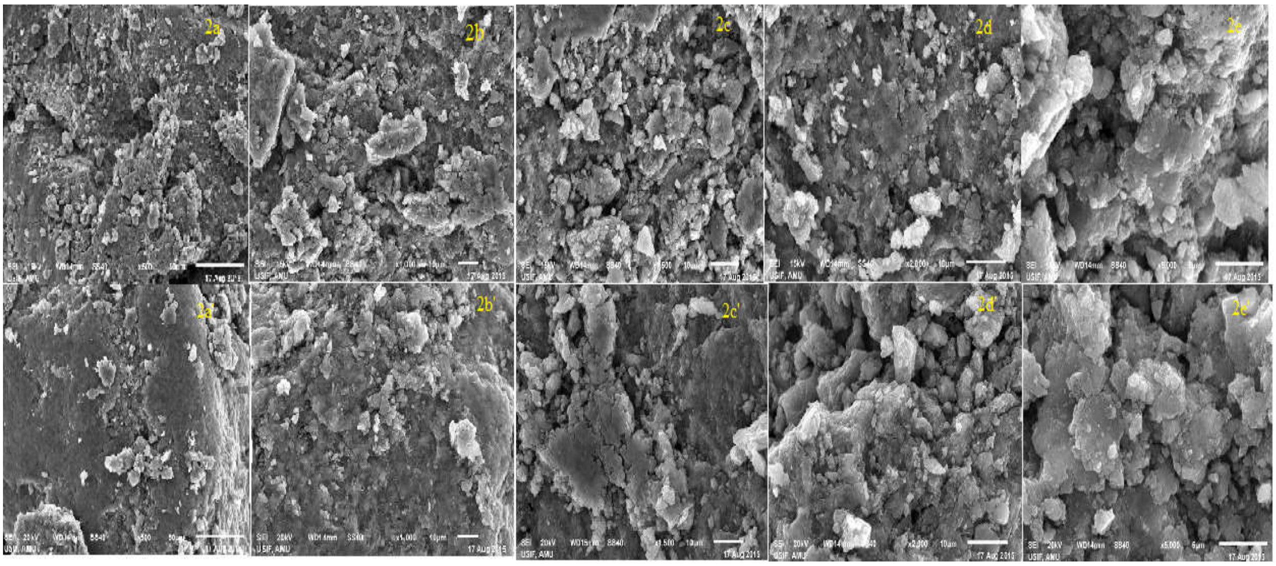


Fig. 2 SEM images of adsorbent PZIP before (2a-2e) adsorption and after adsorption of Pb (II) ion onto PZIP (2a'-2e').

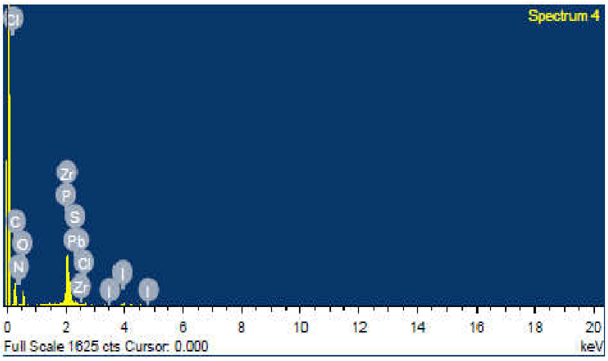


Fig. 3 EDX of adsorbent PZIP before (3a) after Pb (II) adsorption (3b).

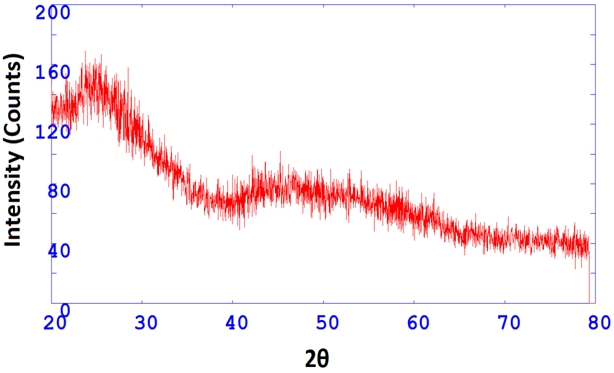


Fig. 4 XRD plot of PAZIP

Effect of contact time

The contact time and concentration effect on the adsorption of Pb(II) ions onto the PZIP (Fig. 5) showed that the adsorption was concentration dependent and increased with increase in initial concentration. The equilibrium adsorption capacities at initial adsorbate concentrations were found to increase from 25-46.98 mgg^{-1}indicating thereby the bigger dynamic potency and a large number of empty surface sites presented for adsorption for the period of the early phase.

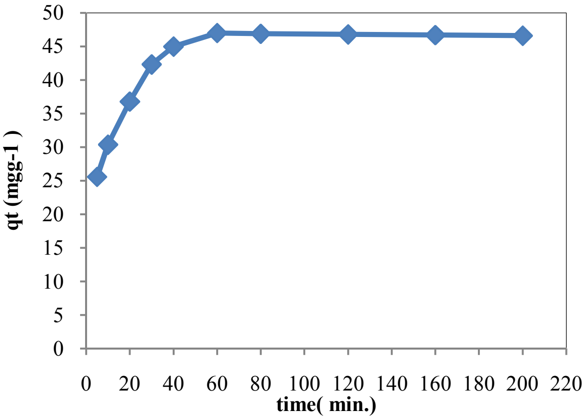


Fig. 5 Effect of contact time on adsorption of Pb (II) onto PZIP (adsorbent dose: 0.02g/L; initial Pb (II) concentration: 50 mg/L; pH:7.0; temperature 303 K).

The initial adsorption rate was high for Pb (II) ion (25 min) and then reduced while approaching near equilibrium. As the time increases lasting available sites were tough to be engaged because of repulsion between the solute molecules on the solid and bulk phases while after fullness of adsorption sites, the adsorption of Pb (II) progressed to equilibrium through pore diffusion mechanism which is a slow process. The time required to attain the equilibrium for the adsorption of Pb (II) was found to be 60 min at initial Pb (II) concentrations of 50 mg/L.

Effect of pH

The adsorption process is influenced by pH of the working solution as it provides positive or negative charge to the surface of adsorbate and adsorbent and also the degree of dissociation of adsorbate molecule. It was observed (Fig.6) that the adsorption capacity of the adsorbent increases with increase in the pH of the aqueous solution.

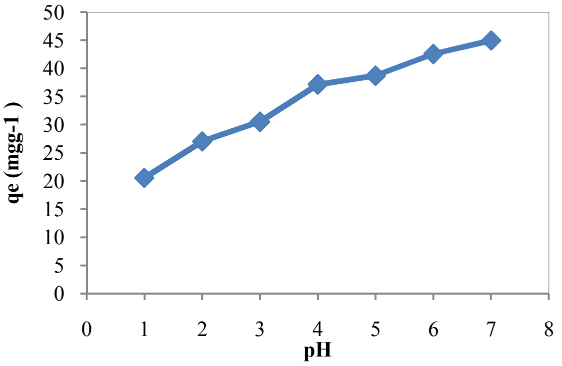


Fig. 6 Effect of pH on adsorption of Pb (II) onto PZIP (adsorbent dose: 0.02g/L; initial Pb (II) concentration: 50 mg/L; pH: 7.0; temperature 303 K).

The maximum adsorption of lead (II) ions on to the surface of adsorbent takes place at pH 7 at room temperature. All the kinetic and thermodynamic experiments were carried out at pH 7. At pH >7.5, lead ion get precipitated in the form of $Pb(OH)_2$ and hence above pH 7 adsorption of Pb(II) ions on polyaniline-Zr(IV)-iodophosphate was not studied [2].

Effect of dose

The quantity of metal ion adsorbed at the surface of adsorbent may be estimated by varying the amount of adsorbent. It was observed (Fig. 7) that the initial percentage of adsorption increases very fast from 25 % to 88 % for PZIP-Pb (II) system, with the increase in PZIP dose from 0.02 to 0.15 g/L. But beyond this value, the percent metal adsorption reached almost at a constant value. The reason for this trend may be because of increase in the adsorbent dose increases the active adsorption sites as quantity of adsorbent particles rises and thus more Pb (II) ion can be attached to their surfaces. The maximum adsorption capacity was found at 0.1g/L of PZIP dose; therefore, it was selected for further experiment.

Kinetics of adsorption

Based on the literature survey, experimental data were tried with different kinetic models such as Lagergren pseudo first order kinetic model, Ho and McKay pseudo second order kinetic model, Elovich model and intra particle diffusion model to investigate controlling mechanism of adsorption of Pb (II) ions on the surface of adsorbent. For this the batch adsorption process was used to study the kinetics as a function of time whilethe other parameters likeconcentration, amount of adsorbent, temperature, shaking speed and pH of the working solution were kept constant for all experiment.

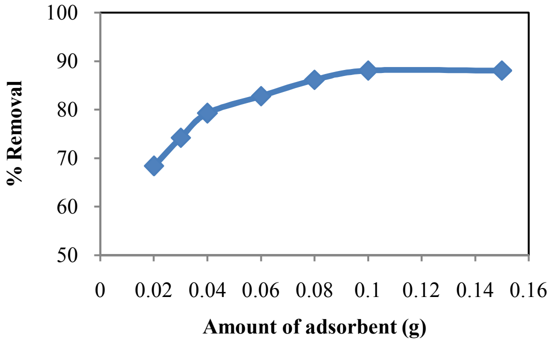


Fig. 7 Effect of adsorbent dose on adsorption of Pb (II) onto PZIP (adsorbent dose: 0.02g/L; initial Pb (II) concentration: 50 mg/L; pH: 7.0; temperature 303 K).

Lagergren pseudo first order kinetics

The Lagergren pseudo first order kinetic modelgenerally expressed by the following Eq.(3)[26].

$$\frac{\partial q_t}{t} = K_1.(q_e \quad q_t) \tag{3}$$

where,q_e and q_t are the adsorption capacities (mgg^{-1}) of the adsorbent at equilibrium and at time t, respectively. The K_1 and t are the Lagergren pseudo-first-order rate constant (min^{-1}), and the time of contact (min), respectively. The integration of equation (3) with the initial condition, $q_t = 0$ at $t = 0$and $q_t = q_t$ at t = t, the equation becomes and yields Eq. (4).

$$\log(q_e \quad q_t) = \log q_e \quad \frac{K_1 \times t}{2.303} \tag{4}$$

The relation between the log of the difference of adsorption capacities at equilibrium and at a particular time was analyzed and the value of K_1 and $q_e$can be calculated from slope and intercept of the plot (Fig. 8) between log ($q_e \quad q_t$) vs. t respectively.

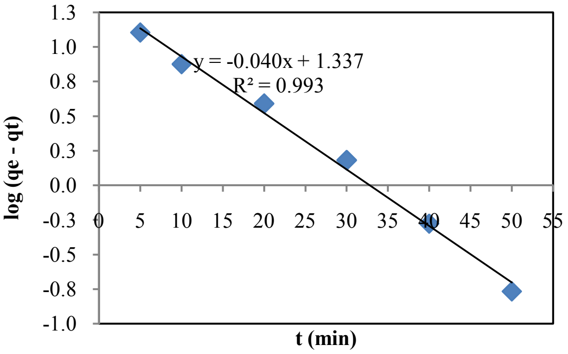


Fig. 8 Pseudo-first order kinetic plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.1 g/L; initial metal ion concentration: 100 mg/L; pH: 7; temperature: 303 K).

Ho and McKay pseudo second order kinetic model

The Ho and Mckaypseudo second order kinetic modelis generally expressed by Eq. (5)[27].

$$\frac{\partial q_e}{\partial t} = K_2(q_e \quad q_t)^2 \tag{5}$$

where, K_2 is the Ho and Mackay pseudo second order rate constant ($gmg^{-1}.min^{-1}$). Integrating Eq.(5) and applying boundary conditions, $q_t = 0$ at t=0 and $q_t = q_t$ at t = t, gives the Eq. (6).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) \times t \qquad (6)$$

The relation of adsorption capacity at particular time interval with respect to time was studied (Fig. 9).

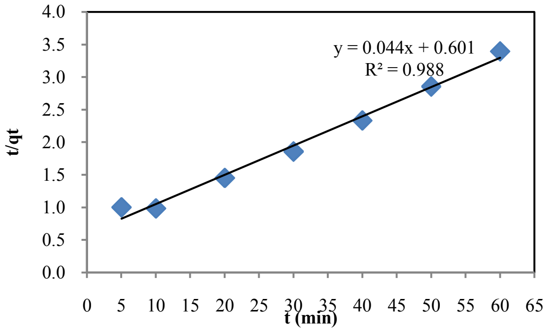


Fig. 9. Pseudo-second order kinetic plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.1 g/L; initial metal ion concentration: 100 mg/L; pH: 7; temperature: 303 K).

The value ofK_2 ($gg^{-1}.min^{-1}$) and q_e (mgg^{-1}) may be obtained from the plot between $\frac{t}{q_t}$ vs. t. The initial sorption rate, $h_{0,2}$ ($mgg^{-1}.min^{-1}$), at t→0 is defined by Eq. (7).

$$h_{0,2} = K_2 q_e^2 \qquad (7)$$

The Eq. (6) can be modified with the help of Eq. (7) and can be expressed by following Eq. (8):

$$\frac{t}{q_t} = \frac{1}{h_{0,2}} + \left(\frac{1}{q_e}\right) \times t \qquad (8)$$

The initial sorption rate $h_{0,2}$ is obtained from the intercept since q_e known from the slope, the second order rate constant K_2 can be determined from the Eq. (7).

Intraparticle diffusion

It is assumed that the mechanism for removal of metal ion by adsorption by a sorbent material is taking place through four steps:

1. Movement of metal ion from bulk solution to the surface of adsorbent (bulk diffusion).
2. The metal ion diffusesto the surface of the adsorbent through boundary layer (film diffusion).
3. Transport of metal ion from the surface to the interior pores of the particle (pore diffusion mechanism or intra-particle diffusion).
4. The adsorption of metal at an active site on the surface of adsorbent by chemical reaction (ion-exchange, complexation and chelation).

The probability of intra particle diffusion conflictinfluencing adsorption was examinedby using the intra particle diffusion model, can be written byfollowing Eq. (9)[28].

$$q_t = K_{id} \times t^{0.5} + I \qquad (9)$$

where,K_{id}, and I arerate constant for intraparticle diffusion ($mgg^{-1}.min^{-1}$) and a constant gives an idea about the thickness of the boundary layer, respectively. If the intercept is larger, the boundary layer effect will be more[2]. If the q_t versus $t^{0.5}$ plot exhibits a straight line and passes through the beginning then the intra-particle diffusion is the only phenomenon that governed the adsorption process, when the plot divides multi-linear characteristic two or more steps has influence on the adsorption process[29]. It is very clear (Fig. 10) that there is a deviation of straight line from the origin and multi-linearity, may be due to the dissimilarity between the rate of mass transfer in the early and last stages of adsorption.

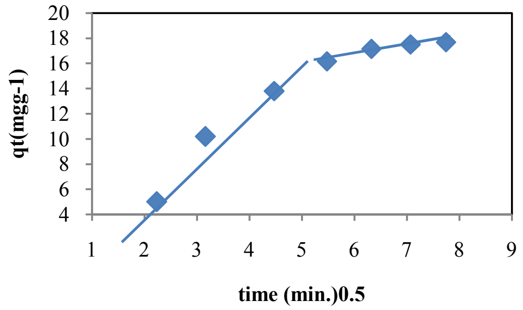


Fig. 10 Intraparticle diffusion plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.1 g/L; initial metal ion concentration: 100 mg/L; pH: 7; temperature: 303 K).

In this view, the steps 1 and 4 are very fast in nature and could not be limiting factor in the rate of adsorption process. The second step may be attributed to boundary layer diffusion of Pb(II). The slow sorption in which the rate-controlling step is the intraparticle diffusion described by the third step. In the final stage, the intraparticle diffusion process became slow since low concentration of Pb(II) remained in the solution. Similar explanations have been reported for the mansonia wood sawdust and polyacrylamide-Zr(IV)-iodate for adsorptive removal of Pb(II)[30, 31].The result obtained for kinetic data are given in Table 1.

Adsorption equilibrium studies

An adsorption isotherm pronounces the relationship between the amounts of adsorbate (metal) adsorbed at the surface of adsorbent and the residual concentration of the metal ion in the solution. There are many isotherm models used to analyze experimental data. These equilibrium isotherm models provideaffinity of the sorbent, the surface properties andunderstanding of the adsorption mechanism. In this work the equilibrium characteristics of adsorption were described by Freundlich, Langmuir, Dubinin–Radushkevich and Temkin isotherm.

Table 1 Kinetic parameters for adsorption of Pb (II) onto PZIP

Adsorption system	q_e^{exp}	**Pseudo-first order**				**Pseudo-second order**					**Intraparticle Diffusion**		
		q_e^{cal}	K_1	$h_{0.1}$	R^2	q_e^{cal}	K_2	$h_{0,2}$	$t_{1/2}$	R^2	K_{id}	C	R^2
PZIP-Pb (II)	17.68	21.72	0.09	1.66	0.99	22.27	0.0033	1.03	10.6	0.98	2.42	2.42	0.88

The Langmuir adsorption isotherm

The Langmuir isotherm considered monolayer adsorption at the surface of adsorbent is based on following assumptions:

1. Due to the involvement of weak physical interaction of forces metal ionare adsorbed at a fixed number of well- defined identical sites on the surface of homogeneous adsorbent that are equally available i.e. each site carry equal no of ion.
2. All sites are equivalent in energy and there is no contact between the adsorbate molecules.

According to this isotherm, sorption takes place at definiteidentical sites within the adsorbent. The general expression of the Langmuir equationcan be written by Eq. (10)[32].

Table 2 Isotherm parameters for adsorption of Pb (II) on PZIP

Adsorption-system	**Langmuir isotherm parameters**				**Freundlich isotherm parameters**		
PZIP-Pb	$\mathbf{q_m}$	**b**	$\mathbf{R_L}$	$\mathbf{R^2}$	$\mathbf{K_f}$	$\mathbf{\frac{1}{n}}$	$\mathbf{R^2}$
q_e^{cal}	17.48	0.04	0.17	0.99	0.57	0.71	0.99
	Temkin isotherm parameters				**Scatchard isotherm parameters**		
17.68	**B**	**b**	**A**	R^2	θ_s°	K_s	R^2
	0.08	31410	1.11	0.99	0.86	0.04	0.96

$$\frac{1}{q_e} = \left(\frac{1}{K_L . q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad (10)$$

where, q_e (mgL^{-1}) is the adsorption capacity at equilibrium, and C_e (mgL^{-1}) is the concentration of Pb (II) in the liquid phase at equilibrium, respectively.$K_L$and q_m are the Langmuir constants.The $q_m$isthe maximum metal uptake (mgg^{-1}) and K_L is reveal to the affinity of the sorbent and the energy of adsorption. The relationbetween $\frac{1}{q_e}$ versus $\frac{1}{C_e}$(Fig. 11) used to determine the Langmuir's parameters. The value of intercept and slope of the plot gives the value ofq_m and $K_L$and are given in Table 2. Anadditionalexploration for the Langmuir equation can be made by dimensionless constant, $R_L$commonly known as separation factor expressed by Eq. (11)[33].

$$R_L = \frac{1}{1 + K_L C_i} \qquad (11)$$

where,K_L is Langmuir constant (Lmg^{-1}) and C_i is the initial metal ion concentration (mgL^{-1}). It gives favorable adsorption when $0<R_L<1$.

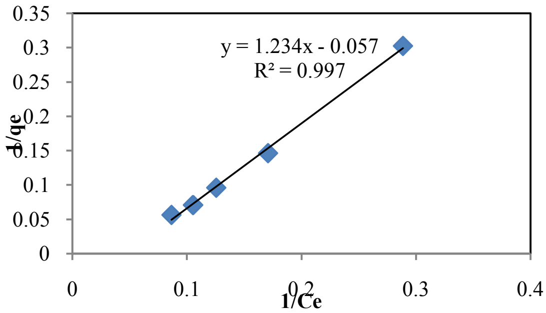


Fig. 11 Langmuir isotherm plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.04 g/L: pH: 7; temperature: 303 K).

In this work the value of R_L was in between 0 and 1 signifying that the adsorption of Pb (II) on the surface of PZIP was favorable. The result from Langmuir isotherm model is given in Table 2.

Freundlich adsorption isotherm

The Freundlich isotherm describes the non-ideal, reversible, adsorption; follow the multilayer adsorption at the heterogeneous surface of adsorbent. As the binding sites at the heterogeneous surface of adsorbent possesses different amount of bond energy. The stronger binding sites are engaged first, and as the time passes towards the completion of adsorption process, adsorption energy falls exponentially. Thus the amount adsorbed in a Freundlich assumption is the summation of adsorption on all sites[34]. The exponential equation of Freundlich expression assumed that as the concentration of the adsorbate increases, the concentration of adsorbate on the surface of adsorbent increases too. Hypothetically, an infinite amount of adsorption can occur in accordance with this expression.

The logarithmic form of the Freundlich isotherm is widely applied in heterogeneous system can be written by Eq. (12)[35].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (12)$$

where, q_e, and C_e, are theadsorption capacity of the adsorbent i.e. metal ion adsorbed at equilibrium time, the concentration of Pb(II) ionin solution at equilibrium, respectively.

K_f(Lg ^{1})signifying the adsorption capacity and n adsorption intensity, respectively. The isotherm constant can be calculated from the intercept and slope of plot between log q_e vs. log C_e(Fig. 12) and are presented in Table 2. On the basis of the high value of the correlation coefficient it may be concluded that the experimental data were also adjustedvery well in Freundlich isotherm model. Similar order of adsorption capacity was observed as in Langmuir isotherm. Since the value of 1/n <1 revealing favorable adsorption for the Pb (II) ions adsorption onto the surface of PZIP[36].

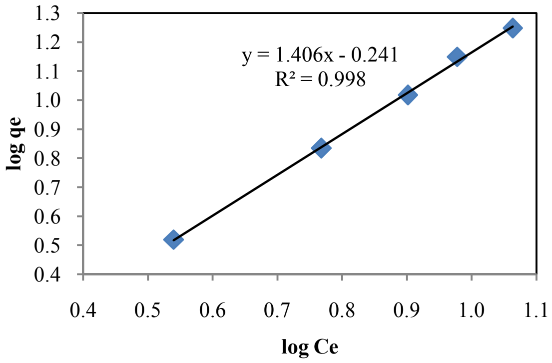


Fig. 12 Freundlich isotherm plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.04 g/L: pH: 7; temperature: 303 K).

Temkin isotherm

The Temkin isotherm adopts that the fall in the heat of adsorption is linear rather than logarithmic, as understood in the Freundlich equation[37]. The general form of Temkin isotherm can be expressed by Eq. (13)[38].

$$q_e = B\ln A + B\ln C_e \qquad (13)$$

where,

$$B = \frac{RT}{A} \qquad (14)$$

where, B, T, R and A are the Temkin isotherm constant (J/mol) related to adsorption heat, the absolute temperature (K), the real gas constant ($Jmol^{-1}K^{-1}$), the Temkin isotherm constant (Lg^{-1}), respectively.The slopes and intercepts of plot q_e vs. $\ln C_e$(Fig. 13) gives the value of B and A respectively. The values of the Temkin constants B, b, A, and R^2 obtained from the plotare given in Table 2.

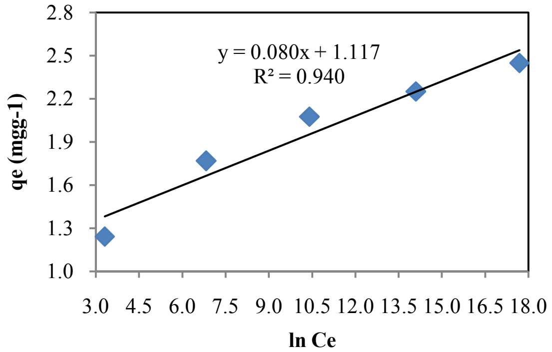


Fig. 13 Temkin isotherm plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.04 g/L: pH: 7; temperature: 303 K).

Scatchard isotherm model

In order to evaluate the affinities of binding sitesparticipating in a particular adsorption process Scatchard isotherm model has been employed. The general equation of the Scatchard isotherm can be written by the following Eq.(15)[39].

$$\frac{q_e}{C_e} = K_s\,(\theta_s^{\circ} \quad q_e) \qquad (15)$$

where,θ_s° andK_s are Scatchard isotherm constant related to adsorption capacity (mg/g) and adsorption constant (L/mg), respectively. The values of θ_s° and K_s were obtained from the intercepts ($K_s\theta_s^{\circ}$) and slopes (K_s) of the plots $\ln q_e$vs.$\ln C_e$(Fig. 14) and are given in Table 2.

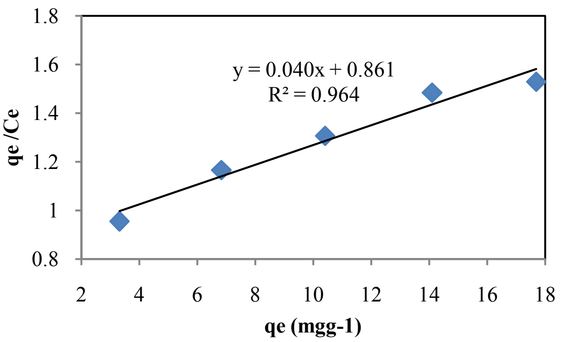


Fig. 14 Scatchard isotherm plots for the adsorption of Pb (II) onto PZIP (Adsorbent dose: 0.04 g/L: pH: 7; temperature: 303 K).

The Scatchard plot tells about the type of relations of adsorbate with adsorbent. Anabnormality from linearity was observed in values of correlation coefficient (R^2) showed more than one type of binding sites were available[40]. It is clear fromthe Table 2 that the adsorption of Pb (II) by polyaniline-Zr (IV)-iodophosphate followed bothadsorption isotherms models, the Freundlich and the Langmuir, so other isotherm models were omitted. However, on the basis regression values, the Freundlich adsorption model is well followed by the system than the Langmuir one. This leads to the conclusion that the surface of the polyaniline-Zr(IV)-iodophosphate is made up of small heterogeneous adsorptivepatches which are alike to each other for adsorption phenomenon[41].

Thermodynamics studies

In order to understand the thermodynamic behavior of Pb(II) adsorption onto the PZIP adsorbent with respect to temperature, standard Gibbs free energy change (G°), the entropy change (S°) and the enthalpy change (H°) were estimated using the following Eq. (16), Eq. (17), and Eq. (18)[42].

$$G^{\circ} = \quad RT\ln K_C \qquad (16)$$

$$K_C = \frac{q_e}{C_e} \qquad (17)$$

$$\ln K_C = \frac{S^{\circ}}{R} + \frac{H^{\circ}}{RT} \qquad (18)$$

where, R, T, and K_C are the ideal gas constant (8.314 $Jmol^{-1}K^{-1}$), the absolute temperature (K), and the thermodynamic equilibrium constant, respectively. $G°$, $H°$ and $S°$ are standard Gibb's free energy ($kJmol^{-1}$), change in standard enthalpy ($kJmol^{-1}$), and change in standard entropy ($Jmol^{-1}K^{-1}$) respectively. The parameter q_e is the amount of Pb (II) adsorbed at equilibrium in mgg^{-1} and C_e is the equilibrium concentration of the solution in mgL^{-1}.

A series of experiment at 303, 213 and 323 K for PZIP- Pb (II) system was performed to see the effect of temperature on adsorption capacities. It was found that the adsorption capacities increased from17.68- 17.91mgg^{-1} for Pb(II) (Fig. 15), as the temperature of metal ion solution increased from 303 – 323 K indicating that the adsorption of Pb(II) onto the PZIP was endothermic in nature.

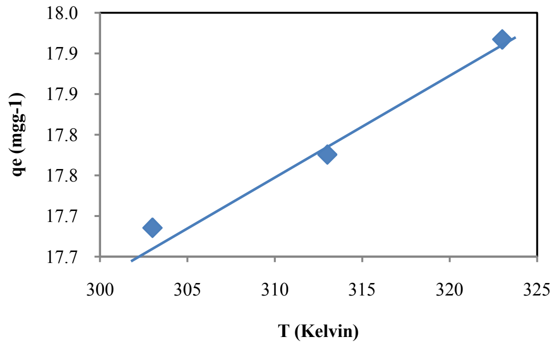


Fig. 15 Effect of temperatures (303K, 313K, 323K) on the adsorption of Pb(II) ion on to PZIP

The intercept and slope of the Van't Hoff plot between $\ln K_C$versus$\frac{1}{T}$(Fig. 16) gives the values of S°and H°. The Gibbs free energy change (G°) was found to be -1.0683, -1.2199, -1.4565, kJ mol^{-1} that reflects the physio-sorption (-20 kJmol^{-1}> G°< 0) for Pb (II) adsorption at 303K, 313K, and 323K respectively[24].

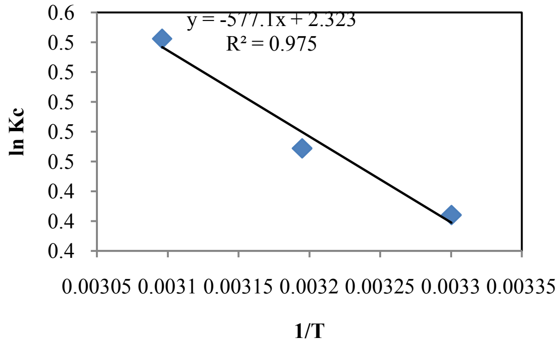


Fig. 16 Van't Hoff plot for the adsorption of Pb(II)

The negative G° values showed the feasibility and spontaneous nature of the adsorption and increment of negativity for G° indicates that the adsorption process is favored at higher temperature and endothermic in nature. The H° parameter was found to be 1454.02 kJmol^{-1} for Pb(II). The positive H° indicates the endothermic nature of the adsorption processes at 303-323K. The S° parameter was found to be 19.320 Jmol^{-1}K^{-1} for Pb(II) adsorption, reflects the affinity of the polyaniline-Zr(IV)-iodophosphate for Pb (II) ions and the increasing randomness at the solid/solution interface as the Pb(II) ions interact with the functional groups on the polyaniline-Zr(IV)-iodophosphate[43-45]. The values of the thermodynamics parameters such as G°, H° and S°, calculated from the Van't Hoff plot are given in Table 3.

Table 3 Thermodynamic parameters for adsorption of Pb (II) ion at different temperature

Adsorption system	**H° (kJmol^{-1})**	**S° (Jmol^{-1}K^{-1})**	**G° (kJmol^{-1})**		
			303 K	**313 K**	**323 K**
PZIP-Pb	1454.02	19.32	(-) 1.06	(-) 1.21	(-) 1.45

Desorption studies

Recovery of the adsorbent makes the treatment process more economical and feasible. For regeneration of the adsorbent, Pb(II) loaded PZIP was treated with 1 M HNO_3 solution for fixedperiod. Treated solution was collected and analyzed for Pb(II) content in filtrate after desorption. The renewal proficiency of the adsorbent was determine by using the following Eq.(19)[46].

$$\% \mathrm{RE} = 100 \times \frac{q_a}{q_b} \tag{19}$$

where, $q_b$is adsorption capacity (mgg^{-1}) of adsorbents before and q_a is the adsorption capacity (mgg^{-1}) of adsorbentsafter regeneration respectively. After three consecutive regeneration cycles the adsorptive removal of PZIP for Pb (II) was found to be ~80 %.

CONCLUSION

In this research work we prepared a novel adsorbent, polyaniline-Zr(IV)-iodophosphate, using convenient Sol-Gel method and successfully employed as an adsorbent for the deduction of Pb (II) from aqueous solution. The adsorbent showing good removal (89.58%) of Pb (II) from aqueous solution at optimum condition of 0.1gL^{-1}, pH =7.0, 60 min of contact time, and 50°C. The experimental data were best fitted to pseudo first order and pseudo second order, and Langmuir and Freundlichsince adsorption capacitiesq_e calculated from models are very close to q_e determined experimentally and also on the basis of regression coefficient values favors the adsorptive removal of Pb (II) by the PZIP. The thermodynamic parameters reflect endothermic, spontaneity, and nature of adsorption was physical. The adsorbent can be regenerated by using 1 M HNO_3 solution. Therefore on the basis above results it may be concluded that the synthesized polyaniline-Zr(IV)-iodophosphate has potential to reduce the concentration of lead from the aqueous solution and can be employed as an effective adsorbent for the treatment of water adulterated with Pb (II).

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